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(54) OPTICAL INFORMATION STORAGE MATERIAL

(71) We, MATSUSHITA ELECTRIC INDUSTRIAL CO. LTD., a Japanese Body Corporate, of 1006 Kadoma, Osaka 571, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is concerned with optical information storage materials, the optical density, or transmissivity, of which can be varied, and with a method of making such materials.

Certain materials are known which have the property of exhibiting two physical states in which the materials have different optical transmissivity. The materials are amorphous and the transition between the two states can be effected by subjecting the materials to electrical, optical or thermal energy. In one of the two states, the material has a so-called non-crystalline bulk structure in which the atoms and molecules of the material, viewed microscopically, are partially ordered, though the material can be seen to have a non-crystalline structure. In this state the material has a low optical density, that is, a higher transmissivity. In the alternative state the material has a crystalline structure and exhibits a relatively high optical density.

It would be advantageous if materials exhibiting these properties could be used successfully as information storage devices, making use of the transitions between the two different optical states, but the materials exhibiting these properties of which we are aware have disadvantages when used as information storage devices. For example, amorphous materials which have the desired properties are multi-component materials such as (Te, Ge, Sb, S) or (Te, Ge, As, Ga). Such materials are chalcogenide composites which easily form a two dimensionally bonded atomic configuration in a glassy state or are composites which are obtained by adding elements which easily form a covalent tetrahedral atomic structure to the chalcogenide composites. These composites have the advantage that they are stable at room temperature in both crystalline and non-crystalline states, but have the disadvantage that their sensitivity is such as to make them unsuited to use as information storage devices. Also, the materials, even as thin films, have a relatively high optical density in their non-crystalline state, so that when used in a manner to give a high contrast ratio between the two states, for example a ratio of greater than 10:1, the read-out efficiency is low, for example less than 10%.

We have now found that films of certain mixed sub-oxides have the desired property of existing in two states having different optical densities, or transmissivities, and of being convertible from one to the other and can be used to form optical information storage materials having better properties than the known materials referred to above.

According to the present invention, we provide an optical information storage material comprising a substrate having deposited thereon a mixed sub-oxide film which is convertible between a low optical density state and a high optical density state by the application of electrical, optical or thermal energy, the mixed sub-oxide comprising at least one first sub-oxide selected from GeO_{x1}, SnO_{x1}, SbO_{x2}, TlO_{x2}, BiO_{x2} and MoO_{x3}, where $O<x1<2.0$, $O<x2<1.5$ and $O<x3<3.0$, and a minor, sensitivity-enhancing amount of at least one second sub-oxide.

When the first sub-oxide is selected from GeO_{x1} and SnO_{x1}, the second sub-

oxide is preferably selected from SbO_{x2}, BiO_{x2}, TeO_{x1} and PbO_{x4}, where x1 and x2 are as defined above and $O<x4<1.0$.

When the first sub-oxide is SbO_{x2}, the second sub-oxide is preferably selected from TeO_{x1}, BO_{x2}, PbO_{x4} and CuO_{x4}, where x1, x2 and x4 are as defined above.

When the first sub-oxide is TlO_{x2}, the second sub-oxide is preferably selected from TeO_{x1}, SnO_{x1}, GeO_{x1}, BO_{x2} and SbO_{x2}, where x1 and x2 are as defined above.

When the first sub-oxide is BiO_{x2}, the second sub-oxide is preferably selected from TeO_{x1}, SnO_{x1} and SbO_{x2}, where x1 and x2 are as defined above.

When the first sub-oxide is MoO_{x3}, the second sub-oxide is preferably selected from PbO_{x4}, SbO_{x2}, BiO_{x2}, TeO_{x1}, BO_{x2}, SnO_{x1} and InO_{x2}, where x1, x2, x3 and x4 are all as defined above.

The present invention also comprises a method of making an optical information storage material according to the invention, which comprises evaporating a solid solution comprising at least one first stoichiometric oxide selected from GeO_2, SnO_2, Sb_2O_3, Tl_2O_3, Bi_2O_3 and MoO_3, and a minor amount of at least one second stoichiometric oxide, the evaporation being carried out in the presence of a reducing element, and depositing the resulting vapour on the substrate to form the mixed oxide film.

According to a further aspect of the invention, there is provided a method of recording information, which comprises imagewise application of electrical, optical or thermal energy to the sub-oxide film of an optical information storage material according to the invention so as to cause conversion from the low optical density state to the high optical density state. This conversion may be viewed by reflectance (when the substrate is generally opaque) or transmission (when the substrate is generally transparent).

In the following description reference will be made to the accompanying drawings in which:

Figure 1 is a diagrammatic cross-sectional view of an optical information storage material according to the invention;

Figure 2 is an elevational view illustrating diagrammatically a method of recording information on the material illustrated in Figure 1;

Figure 3 is an elevational view showing diagrammatically an alternative method of recording information on the material illustrated in Figure 1; and

Figures 5 to 7 are graphs showing the relationship between light transmissivity and wavelength for different forms of material in accordance with the invention.

The information storage device shown in Figure 1 comprises a substrate 10 on which is deposited a mixed sub-oxide film 11, as described above. If desired, a layer of protective lacquer 12 or the like can be provided on the film 11.

The film 11 is preferably prepared by vacuum evaporation of the solid solution as specified above, vacuum evaporation being effected, for example, by heating under vacuum in a quartz or platinum crucible, in the presence of a reducing element. If such a reducing element is not used, the deposited (stoichiometric) film does not exhibit suitable properties for use as a recording material. Such films may be white or transparent, are not light absorptive, and do not exhibit the desired optical properties. However, if the oxides are vaporised under the appropriate deoxidizing conditions, (that is, in the presence of the reducing element) the deposited film is in the form of sub-oxides, with the desired properties. Suitable reducing elements include W, Mo, Cr and Fe.

The solid solution used in this method may be made, for example, by forming a powder mixture comprising the stoichiometric oxides, melting the mixture, holding the mixture in the molten state for 3 to 4 hours and quenching the melt.

A suitable form of apparatus for carrying out the deposition is shown diagrammatically in Figure 4. In this Figure a vacuum chamber 15 is employed, in which the appropriate degree of vacuum is produced, by means not shown. A substrate 16 to be coated is positioned on a suitable support 17 over a vapour source which includes a crucible 18 containing the vaporisable material 19. The crucible is surrounded by an electric heater 20, the heater being connected to terminals 21 and 22, to which an external power supply 23 is connected externally. The material 19 in the crucible is vaporised, and deposits as a film 24 upon the surface of the substrate 16.

The appropriate deoxidizing conditions can be obtained by using a crucible 18 made of Mo or W. The vacuum pressure is not critical; a pressure of 10^{-3} mmHg to 10^{-6} mmHg can be used, but departures from the specified range do not result in substantial change of properties of the deposited layer 24 of the sub-oxide. A typical pressure is about 5×10^{-5} mmHg.

The substrate 16 can be of any suitable material or shape. It can be, for example transparent polyester sheet, polytetrafluorethylene, glass or paper; the substrate may be in the form of a sheet, but can also be in the form of a drum or disc or other configuration appropriate to its use as an information storage device.

With the exception of the films of Mo sub-oxide, the films produced in the manner described are for the most part of a pale brown colour and have a light transmissivity which increases with increasing wavelength, over the range of 3500Å to 1 μ. The film of Mo sub-oxide is pale blue in appearance and has a light transmissivity which shows a minimum in the range of 6000 to 9000Å.

The thickness of the film is generally from 300 to 8000Å.

The transitions between the states of the material of the film for the purpose of optical recording or otherwise, can be effected by means of a xenon flash tube, infra-red lamp or by laser, or by direct contact heating by means of a suitable heating device. The sensitivity for optical recording is affected by the thermal properties of the substrate; for example, the thinner the base material the greater the sensitivity exhibited by the film. The effect appears to be due to the fact that the thinner the substrate and the lower its thermal capacity, the more rapidly can its temperature be raised. This appears also to be borne out by the fact that where the state of the material is varied by exposing it to light, for example by means of the xenon flash, the shorter the duration of the flash used the better is the recording efficiency; this would be explained by the fact that during the shorter time, there is less possibility for loss of temperature from the film into the substrate by heat diffusion.

Materials made in the manner described can be used for information storage, for example in audio or video recording, data storage and the like.

Any suitable methods of recording can be adopted, and two examples are indicated in Figures 2 and 3.

In Figure 2, the optical device, comprising substrate 10 bearing the mixed sub-oxide film 11 is positioned beneath an image transparency or mask 30. A flash tube 31, such as a xenon tube is positioned above the transparency or mask. When the flash tube is fired, the pattern of the transparency or mask 30 is transferred to the film 11.

Figure 3 shows diagrammatically a method of producing an image in the optical material by a method involving scanning. In Figure 3, a laser diode 32 is used, such as a gallium arsenide injection laser diode, which emits radiation at a wavelength of 9040Å. The radiation pattern from such a diode normally has a relatively large beam spread and an optical system can then be used to focus the radiation upon the surface of the film 11 on substrate 10. As shown, a first lens 33 is used to produce a substantially parallel beam of radiation 34, which is then focussed by a further lens 35 into a micro spot focus on the film 11 at the point 36. The image pattern is built up by a scanning micro spot 36 over the surface of the film 11, with appropriate modulation of the laser beam from diode 32.

The resultant image is in the form of the film with regions of different transmissivity and so the recorded information can be retrieved by passing light through the film and detecting the transmitted light; alternatively, with appropriate modification, the recorded information can be retrieved by detecting the amount of light reflected from the storage material.

In order that the invention may be more fully understood, the following [illegible] are given by way of illustration only.

EXAMPLE 1

In this example the starting material used was GeO_2 having a tetragonal crystalline structure, with a melting temperature of 1086°C. This GeO_2, in powder form, was mixed with another powdered oxide, which is indicated by M_1, and a powdered reducing element, which is represented by R. The proportions of these basic materials used could be represented by the expression:—

$$[(GeO_2)_{100-y1}(M_1)_{y1}]_{100-z1}R_{z1},$$

where y1 and z1 are the respective molar percentages and where $O<y1<100$ and $O<z1<100$.

The oxide M_1 was one or more of the materials PbO, Sb_2O_3, Bi_2O_3 and TeO_2 and the reducing element R was one or more of the elements Cr, Fe, W and Mn.

The apparatus used was of the type shown in Figure 4. The mixture of GeO_2 powder, the oxide M_1 and the reducing element R was placed in a crucible 18. The

appropriate vacuum was established in chamber 15 and power supplied to the heater element 20 from source 23 to raise the temperature of the material in the crucible. The temperature employed depended upon the nature of M_1, but was in the range from 700°C to 1200°C in each case. The temperature used was sufficient to cause the mixture to melt and react, and to create a vapour, which was deposited as a mixed sub-oxide film upon the surface of the substrate.

Depending upon the additive material used the deposited film had one of the following compositions:—

$(GeO_{x1})_{100-y1}(PbO_{x4})_{y1}$; (a2, a6)

$(GeO_{x1})_{100-y1}(SbO_{x2})_{y1}$; (a3, a7)

$(GeO_{x1})_{100-y1}(BiO_{x2})_{y1}$; (a4, a8)

$(GeO_{x1})_{100-y1}(TeO_{x1})_{y1}$; (a1, a5)

where $O<y1<100$, and x1, x2 and x4 are as defined above.

Figure 5 is a graph showing the spectral transmissivity of the resultant films. In Figure 5 curves a1 to a4 relate to material in the higher state of transmissivity, which may be that in which no information is recorded and curves a5 to a8 are for the same films after they have been brought to their second state, for example that in which data has been recorded. As indicated above, curves a1 and a5 relate to the material in which TeO_2 is used; curves a2 and a6 relate to the material using PbO: curves a3 and a7 to relate to the material using Sb_2O_3 and curves a4 and a8 relate to the material using Bi_2O_3. The curves all relate to materials in which the proportion of the oxide other than GeO_2 was 20 mole %.

The materials made as described above had good properties for use as information storage material.

(1) In the initial state, corresponding to curves a1 to a4, the light transmissivity is about three times as great as that of other materials of which we are aware, described above. The transmissivity in the second state, corresponding to curves a5 to a8, is about the same as that of the other materials of which we are aware, so that the resultant change of contrast is approximately three times that previously attainable.

(2) The magnitude of the change of transmissivity is about three times that of the comparable material because the transmissivity of the material in its initial state is about three times as great as that of the comparable material.

(3) The mechanical strength and durability of the device is good, due to good adherence between the surface of the substrate and the sub-oxide film.

(4) The optical properties of the material are stable in air, when exposed to room lighting.

EXAMPLE 2

In this example powdered orthorhombic Sb_2O_3 of melting temperature 656°C was mixed with another powdered oxide M_2 and a reducing element R, as represented by the following formula:

$$[(Sb_2O_3)_{100-y2}(M_2)_{y2}]_{100-z2}R_{z2}.$$

In this expression y2 and z2 are the molar percentages, and $O<y2<100$ and $O<z2<100$. The oxide represented by M_2 was at least one of the materials TeO_2, CuO, PbO and B_2O_3, and the reducing element R was at least one of the elements Mn, W, Fe and Cr.

The powdered mixture was heated to a temperature in the range from 600°C to 1000°C, depending upon the oxide M_2.

As in Example 1, the mixture was brought to melting temperature, causing the materials to react, and giving rise to the deposit of the mixed sub-oxide on the surface of the substrate.

Depending upon the additive material used, the deposited film had one of the following compositions:—

$(SbO_{x1})_{100-y2}(PbO_{x4})_{y2}$; (c3, c7)

$(SbO_{x1})_{100-y2}(TeO_{x1})_{y2}$; (c1, c5)

$(SbO_{x1})_{100-y2}(CuO_{x4})_{y2}$: (c2, c6)

$(SbO_{x1})_{100-y2}(BO_{x2})_{y2}$: (c4, c8)

where $O<y2<100$ and x1, x2 and x4 are as defined above.

Figure 6 is a graph, similar to Figure 5, showing the relationship between light transmissivity and wavelength for devices using the materials described. In Figure 6, curves c1 to c4 are for the initial condition of the materials, as might be with nothing recording thereon, and curves c5 to c8 are for the corresponding samples in their second state in which information may have been recorded. As indicated above, curves c3 and c7 relate to the material in which PbO was used, curves c1 and c5 to material in which TeO_2 was used, curves c2 and c6 to the material in which CuO was used and curves c4 and c8 to the material in which Sb_2O_3 was used.

The materials described had the following advantages over comparable materials of which we are aware.

(1) The sensitivity was about three times as great as comparable materials.

(2) In the initial state, corresponding to that in which no information is recorded upon it, the light transmissivity is about twice that of the comparable material, which means that a higher contrast ratio by a factor of 2 can be obtained.

(3) The optical properties of the material are stable in air, under conditions of room lighting.

EXAMPLE 3

In this example, powdered orthorhombic MoO_3, of vaporising temperature 795°C was mixed with another oxide M_3 and a reducing element R, as represented by the following expression:

$$[(MoO_3)_{100-y3}(M_3)_{y3}]_{100-z3}R_{z3}$$

In this expression y3 and z3 are the molar percentages and $O<y3<100$ and $O<z3<100$. The oxide M_3 consisted of at least one of PbO, In_2O_3, SnO, B_2O_3, Bi_2O_3, TeO_2 and Sb_2O_3 and the reducing element R was at least one of the elements Cr, Fe, W and Mn.

As in Example 1, the mixture was heated in a crucible as indicated in Figure 4, to a temperature in the range from 700°C to 1000°C, depending upon the oxide M_3 used. The mixture melted and reacted and a film of the mixed sub-oxide was deposited upon the substrate.

The deposited film produced in this Example had one of the following compositions, depending upon the additive material used.

$(MoO_{x3})_{100-y3}(SbO_{x2})_{y3}$: (e3, e7)

$(MoO_{x3})_{100-y3}(BiO_{x2})_{y3}$: (e4, e8)

$(MoO_{x3})_{100-y3}(TeO_{x3})_{y3}$: (e1, e5)

$(MoO_{x3})_{100-y3}(BO_{x2})_{y3}$: (e2, e6)

where $O<y3<100$ and x2 and x3 are as defined above.

In their initial condition, before energy was applied to them to change them to their alternative state, and as they might be before information was recorded upon them, these films had a pale blue colour. When exposed to light, such as they might be for the storage of information, the colour changed to a dark blue.

Figure 7 is a graph showing the relationship between light transmissivity and wavelength for the materials described in this Example. In Figure 7, curves e1 to e4 are for the samples in their initial condition, as they might be before recording and curves e5 to e8 are for the corresponding samples in their alternative state and as they might be after having been used for the storage of information. As indicated above, curves e1 and e5 relate to the material in which TeO_2 was used; curves e2 and e6 are for the material in which B_2O_3 was used: curves e3 and e7 are for the material in which Sb_2O_3 was used and curves e4 and e8 are for the material in which Bi_2O_3 was used.

The materials of this example have advantages over comparable materials, as follows:

(1) It is possible to obtain a large change of optical transmissivity, since in the

initial state, before recording, the light transmissivity is about twice that of the comparable material, whilst the transmissivity in the recorded state is about the same as that of the comparable material.

(2) A film based on MoO_{x3} exhibits a relatively large optical absorption coefficient for infra-red wavelengths for example light of a wavelength of about 8000A such as that produced by laser diodes, so that this radiation can be used for recording or for retrieving optical information from a film of the material.

EXAMPLE 4

In this Example, the method adopted was substantially that described in Examples 1 and 2 above, but using as the first oxide SnO_2 of tetragonal crystalline structure, with a melting point of 1127°C. The first oxide was used with a second oxide M_4 and a reducing element R, as represented by the expression

$$[(SnO_2)_{100-y4}(M_4)_{y4}]_{100-z4}R_{z4}$$

where y4 and z4 are the molar percentages and $O<y4<100$ and $O<z4<100$. The oxide M_4 consisted of at least one of TeO_2, PbO, Bi_2O_3 and Sb_2O_3. The reducing element consisted of at least one of the elements Mn, W, Fe and Cr.

The materials were used to produce the film of mixed sub-oxide using the method adopted for GeO_2, as described above.

The deposited film of sub-oxide was of pale yellow colour, with a transmissivity for visible light between about 60 and 80%. When subjected to appropriate optical or thermal energy, the coefficient of transmissivity could be reduced to 10%, and the treated portion became dark coloured.

EXAMPLE 5

The method of Examples 1 and 2 was repeated, using as the first oxide hexagonal Tl_2O_3 of melting point 715°C, together with a second oxide M_5 and a reducing element R, used in proportions given by the expression

$$[(Tl_2O_3)_{100-y5}(M_5)_{y5}]_{100-z5}R_{z5}$$

where x and y are the molar percentages and $O<y5<100$ and $O<z5<100$. The oxide M_5 was at least one of TeO_2, B_2O_3, GeO_2, Sb_2O_3 and SnO. The reducing element R was at least one of the elements Mn, W, Fe, Cr.

The vapour deposition of the sub-oxide film was effected using the method adopted for the material Sb_2O_3 described above. The deposited film was of pale brown colour, and its transmissivity was from 40 to 80% for a range of wavelengths from 6000A to 1.2 micron.

The film thus made exhibited a high sensitivity. When given a short exposure, of less than one second, to a projector lamp the film became darker in a manner which was suitable for use as an information storage material.

WHAT WE CLAIM IS:—

1. An optical information storage material comprising a substrate having deposited thereon a mixed sub-oxide film which is convertible between a low optical density state and a high optical density state by the application of electrical, optical or thermal energy, the mixed sub-oxide comprising at least one first sub-oxide selected from GeO_{x1}, SnO_{x1}, SbO_{x2}, TlO_{x2}, BiO_{x2} and MoO_{x3}, where $O<x1<2.0$, $O<x2<1.5$ and $O<x3<3.0$, and a minor, sensitivity-enhancing amount of at least one second sub-oxide.

2. An optical information storage material according to Claim 1, in which the first sub-oxide is selected from GeO_{x1} and SnO_{x1} and the second sub-oxide is selected from SbO_{x2}, BiO_{x2}, TeO_{x1} and PbO_{x4}, where x1 and x2 are as defined in Claim 1 and $O<x4<1.0$.

3. An optical information storage material according to Claim 1, in which the first sub-oxide is SbO_{x2} and the second sub-oxide is selected from TeO_{x1}, BO_{x2}, PbO_{x4} and CuO_{x4}, where x1 and x2 are as defined in Claim 1 and x4 is as defined in Claim 2.

4. An optical information storage material according to Claim 1, in which the first sub-oxide is TlO_{x2} and the second sub-oxide is selected from TeO_{x1}, SnO_{x1}, GeO_{x1}, BO_{x2} and SbO_{x2}, where x1 and x2 are as defined in Claim 1.

5. An optical information storage material according to Claim 1, in which the

first sub-oxide is BiO_{x2} and the second sub-oxide is selected from TeO_{x1}, SnO_{x1} and SbO_{x2}, where x1 and x2 are as defined in Claim 1.

6. An optical information storage material according to Claim 1, in which the first sub-oxide is MoO_{x3} and the second sub-oxide is selected from PbO_{x4}, SbO_{x2}, BiO_{x2}, TeO_{x1}, BO_{x2}, SnO_{x1} and InO_{x2}, where x1, x2 and x3 are as defined in Claim 4 and x4 is as defined in Claim 2.

7. An optical information storage material according to any of Claims 1 to 6, in which the film has a protective layer thereon.

8. An optical information storage material according to Claim 1, substantially as herein described in any of the Examples.

9. A method of making an optical information storage material according to any of Claims 1 to 6, which comprises evaporating a solid solution comprising at least one first stoichiometric oxide selected from GeO_2, SnO_2, Sb_2O_3, Tl_2O_3, Bi_2O_3 and MoO_3, and a minor amount of at least one second stoichiometric oxide, the evaporation being carried out in the presence of a reducing element; and depositing the resulting vapour on the substrate to form the mixed sub-oxide film.

10. A method according to Claim 9, in which the reducing agent is present in the solid solution.

11. A method according to Claim 9, substantially as herein described in any of the Examples.

12. A method of recording information, which comprises imagewise application of electrical, optical or thermal energy to the sub-oxide film of an optical information storage material according to any of Claims 1 to 7 so as to cause conversion from the low optical density state to the high optical density state.

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1563513 COMPLETE SPECIFICATION
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Sheet 1

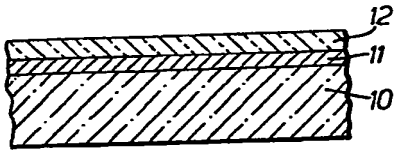


FIG.1.

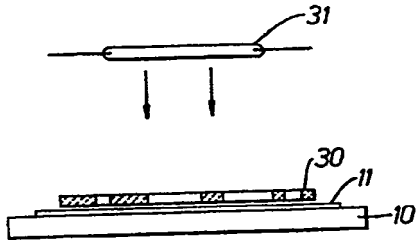


FIG.2.

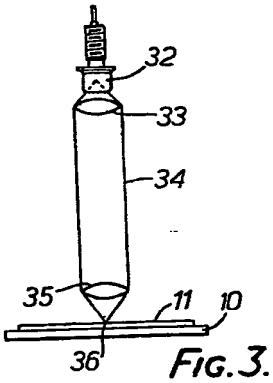
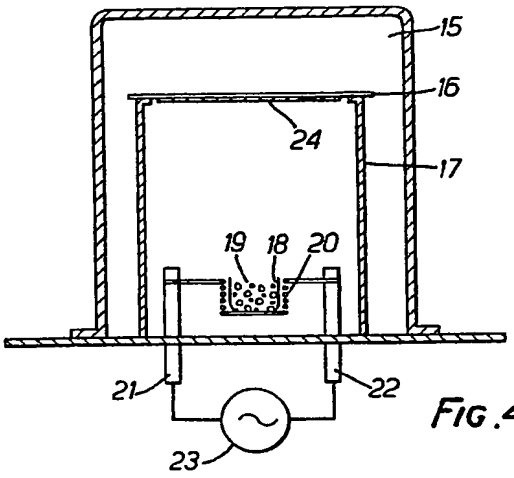


FIG.3.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24
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18
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23

FIG. 4.

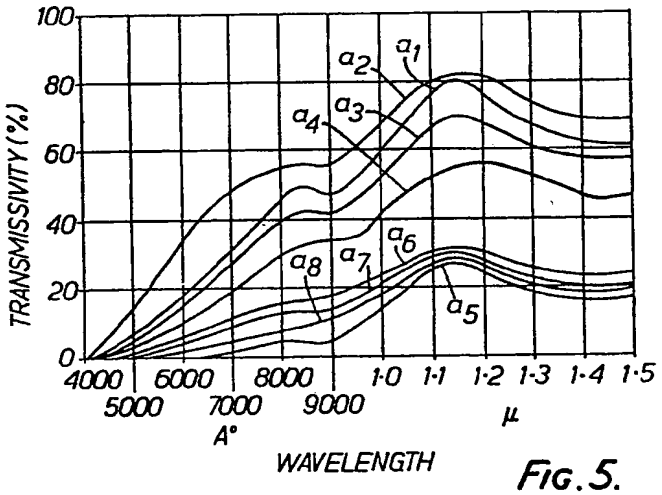
100
80
60
40
20
0
TRANSMISSIVITY (%)
a1
a2
a3
a4
a5
a6
a7
a8
4000
5000
6000
7000
8000
9000
A°
1·0
1·1
1·2
1·3
1·4
1·5
μ
WAVELENGTH

FIG. 5.

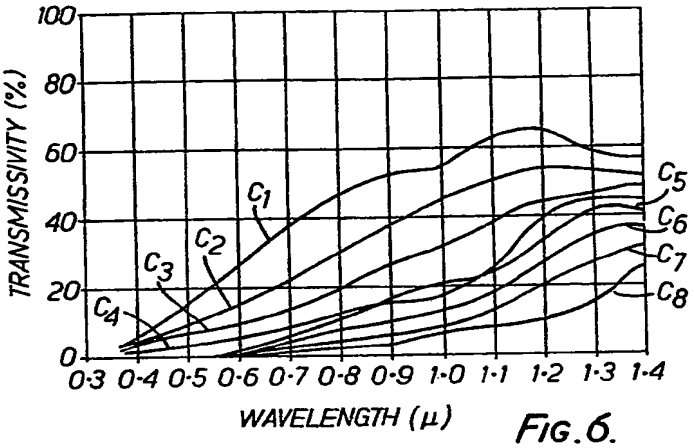

FIG. 6.

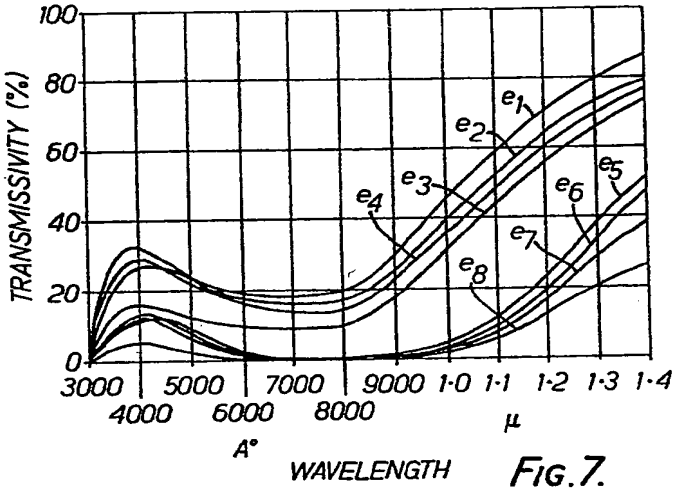

FIG. 7.